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Separation and Determination of Tin, Arsenic & Antimony

Chemistry

B. S.

1902

A New Method for the Separation and Determination of Tin, Arsenic and Antimony with Special Reference to Complex Alloys

BY

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN CHEMISTRY

COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

1902

UNIVERSITY OF ILLINOIS

May 31 1902

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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ENTITLED A New Method for the Separation and Determination of Tin, Arsenic and Antimony

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE

OF Bachelor of Arts.

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A METHOD FOR THE SEPARATION AND DETERMINATION OF LEAD, TIN, ARSENIC AND ANTIMONY WITH SPECIAL REFERENCE TO COMPLEX ALLOYS.

Looking over chemical literature we find that much work has been done on the separation and estimation of Lead, tin, arsenic and antimony. Some of the old methods are still in use, others modify them in their use today, while entirely new ones are constantly being devised.

Drown's method depends upon the volatilization of the chlorides of tin, arsenic and antimony and absorption in potassium bromide; arsenic is distilled from the potassium bromide solution and the tin and antimony separated according to Garnot's method.

Garnot's method, $\overset{\mathrm{I}}{R_1}$p, consists in treating a neutral hydrochloric acid solution of tin and antimony with excess of oxalic acid, to keep back the tin and adding sodium thio-sulphate, when the sulphide of antimony comes down.

Another method, $\overset{\mathrm{II}}{R_2}$, depends upon converting the sulphides of tin, arsenic and antimony into their oxy-salts by boiling with sodium sulphide and cupric oxide.

Bunsen, $\overset{\mathrm{III}}{R_3}$, separates arsenic from antimony by dissolving the sulphides in potassium hydroxide and volatilizing the arsenic by means of chlorine gas. There are many other volatilization methods, those for volatilizing only the arsenic and separating the tin and antimony in some other way, as taking advantage of the insolubility of sodium metantimoniate, oxalic acid to keep back the

tin, and volumetric methods; or by volatilizing all those and collecting in a suitable absorbing liquid. This last does not necessitate the separation of those sulphides first, but can be done in the presence of all the second group metals.

G. Kassner,[IV] dissolves the sulphides of tin, arsenic and antimony in sodium peroxide. Upon acidifying tin oxide comes down and by longer boiling and addition of alcohol pyroantimonic acid separates out.

Clarke's Process,[V] depends upon the fact that tin will not precipitate with hydrogen sulphide from a hot solution containing excess of oxalic acid.

H. N. Warren,[VI] dissolves the sulphides in aqua regia, evaporates nearly to dryness, dilutes with dilute hydrochloric acid and adds excess of potassium ferro-cyanide. The tin is precipitated while the antimony remains in solution.

A new method,[VII] depends upon the insolubility of tin sulphide and easy solubility of the sulphides of arsenic and antimony in lime water.

There are several volumetric methods for arsenic and antimony, for example, oxidation in an alkaline solution is taken advantage of in Fres. Z.A.C. Yahr. 32, p. 415:

$$As_2O_3 + 2H_2O + 4I = As_2O_5 + 4HI$$

$$Sb_2O_3 + 2H_2O + 4I = Sb_2O_5 + 4HI$$

Volumetric antimony in the presence of tin:[VIII] antimony tetrachloride is reduced to the di-chloride by hydriodic acid liberating iodine while the tin tetra-chloride is not reduced.

Antimonic acid and oxide and the tri and pentachloride can easily be distinguished by their behavior towards hydriodic acid. The "ic" form in a hydrochloric acid solution, separates two atoms of iodine for each atom of antimony. Stannic acid and chlorides do not do this. IX

Volumetric estimation of antimony:

$$5Sb_2O_3 + 2IO_5 = 5Sb_2O_5 + 2I_2$$ X

XI

Weil's process for volumetric antimony: Stannous chloride instantly converts antimonic chloride into the "ous" form. Both are soluble and colorless. Add to the antimonic chloride solution a green volume of standard copper solution, then a large excess of hydrochloric acid. This gives a greenish-yellow coloration and the volume of tin solution required to decolorize gives the factor.

Volumetric determination of antimony by means of permanganate: XII Antimony is precipitated as sulphide in excess of oxalic acid, to keep back the tin, and dissolved in concentrated hydrochloric acid; titrate with permanganate:

$$5SbCl_3 + 16HCl + 2KMnO_4 = 5SbCl_5 + 2KCl + 2MnCl_2 + 8H_2O.$$

It will be seen that most of these methods involve the use of yellow ammonium sulphide to separate the sulphides of tin, arsenic and antimony from the rest of the group. Not only is this a tedious process as far as time for complete extraction is concerned, but copper and bismuth sulphides are soluble in this medium to some extent. According to the Analyst, XIII 5.71% of the total copper is soluble in yellow ammonium sulphide, insoluble in colorless ammonium sulphide, but when this is used the tin must first be

thoroughly oxidized or chlorinated. Professor Stillman in recent articles, has shown bismuth sulphide to be soluble to a great extent in ammonium sulphide. In the case of magnolia metal, probably the most advertized of all alloys and containing lead 80%, tin 4.75%, antimony 15% and bismuth .25%, ordinary treatment of a gram of substance would result in a loss of 3% of the bismuth present.

The method often used in analyzing alloys -bringing down with strong nitric acid, the metastannic acid being insoluble- is also inaccurate.

W. E. Garrigues, XIV says "When an alloy is treated with nitric acid, a more or less white residue remains. This residue contains all the tin, part of the antimony, iron, arsenic, phosphorous, copper and lead, the last two only in small amounts, but the copper often amounting to several miligrams". He recommends fusion with sodium thiosulphate to free iron, copper and lead from tin and antimony.

In this work an attempt at a new method was made with a view to the possible use of alkaline peroxides to replace the alkaline sulphides for these reasons:

1. It is desirable to avoid the use of ammonium sulphide because of the time and inaccuracies involved. The distillation methods are not applicable to technical work owing to the elaborate apparatus and length of time involved.

2. The proposed reagents dissolve the sulphides and transform them into the oxy instead of the sulpho salts, thus bringing them into forms most suitable for further separation. XV + XVI.

The scheme at first intended to be followed was to use sodium peroxide and thus bring lead into the subgroup including tin, arsenic and antimony. Sodium peroxide dissolved the four sulphides but on standing tin was thrown down. It was thought that dissolving in KOH and then oxidizing with sodium peroxide, thus bringing in the lead, would get around the difficulty, but again tin was precipitated.

Since KOH dissolved the sulphides of tin, arsenic and antimony so easily and nicely, it was decided to leave lead out of the subgroup and work only with the three others using KOH alone as the solvent and oxidizing with hydrogen peroxide. Strong KOH attacked the lead sulphide slight and also brought down the tin, arsenic and antimony as oxides. Different strengths KOH were tried and it was found that a 1% solution with a little hydrogen sulphide water, dissolved no lead sulphide, but dissolved the other sulphides easily with the exception of stannous sulphide which must first be oxidized. An interesting point came out here when it was found that hydrogen peroxide oxidized stannous tin to the "ic" form in an acid medium when usually it is reducing in this medium. With the 1% KOH treatment the solution remained clear even after long boiling; later it was found that a 1/2% KOH solution was the right strength, the 1% still bringing down the tin on heating.

Precipitating the tin from the oxidized solution was next tried. Sulphuric acid alone precipitated tin completely, antimony in part and arsenic not at all. To keep back the antimony was then the question and it was found that a large excess of ammonium hydroxide and chlorine-free hydrogen peroxide, not only held back

The scheme of first attempted to be followed was to use sodium peroxide and thus throw lead into the sub-group (sulfo-tin, arsenic and antimony. Sodium peroxide dissolved the sulphides but on standing tin was thrown down. It was thought that dissolving in HCl and then oxidizing with sodium peroxide, then bringing to the test, would get around the difficulty, but still tin was precipitated.

Since HCl dissolved the sulphides of tin, arsenic and antimony so easily and cleanly, it was decided to leave lead out of the subgroup and work only with the three others using HCl alone as the solvent and oxidizing with hydrogen peroxide. Strong HCl extracts the lead sulphide might and also brought down the tin, arsenic and antimony as stated. Different strengths of HCl were tried and it was found that a 1% solution with a little hydrogen sulphide water dissolved no lead sulphide, but dissolved the other sulphides easily with the exception of stannous sulphide which must first be oxidized. An interesting point came out here when it was found that hydrogen peroxide oxidized stannous tin to the "ic" form in acid medium when usually it is reducing in this medium. With HCl 1% for instance the solution remained clear even after long standing; later it was found that a 4/10 HCl solution was the right strength, the 1% still bringing down the tin on heating.

Precipitating the tin from the alkaline solution was then tried. Sulfuric acid alone precipitated tin completely, antimony in part and arsenic not at all. To keep back the antimony was the question and it was found that a large excess of ammonium carbonate and sulfide-free sodium sulfide crystals, was only half for

the antimony but also allowed complete precipitation of the tin, though in a difficultly filtering condition.

Hydrochloric and nitric acids only caused turbidness in the case of tin, the $K_2Sb_2O_5$ and $K_2As_2O_5$ remaining clear. Acetic acid alone precipitated the tin completely and antimony partially, but in the presence of ammonium acetate, antimony and arsenic remained clear, while the tin was precipitated completely, though hard to filter. $Mn(OH)_3$ caused a clear and more rapid filtration, but was unsatisfactory on account of the tediousness and little gained. Precipitation as zinc stannate was not quite complete while a large part of the antimony came down; with manganese the same results were obtained.

The acetic acid precipitation was so far the best, but as the precipitate was not granular, it was thought that in some way it could be changed to the oxide. Precipitation in the hot and cold and other variable conditions had no effect, so something else was tried, ammonium persulphate, with the idea that a less hydrated form as stannic oxide would be formed:

$$K_2SnO_3 + 2NH_4SO_4 = SnO_2 + K_2SO_4 + (NH_4)_2SO_4 + O$$

The oxide is not precipitated, but the acid in a good filtering condition is and that completely in both a faintly alkaline and in an acid medium, although when acid it does not filter as well, so that it is best to add the persulphate in moderate quantities and heat until nearly neutral, for upon boiling long the persulphate, decomposing the water, forms an acid medium. $K_2Sb_2O_5$ remains clear until the acid point is reached when the antimony begins to come down, but if ammonium acetate is present the solution remains clear

and as this does not affect the tin precipitation it can be used. $K_2As_2O_5$ remains clear under either of the above conditions.

Here then would have been a method of the mixed sulphides of an alloy behaved like the single sulphides. The peculiar behavior of tin came up in the work at this stage. Stannic sulphide had always been dissolved in 1 and even 2% KOH and the resulting solution remained clear even after long heating; but now a 1% solution precipitated the tin as soon as solution was effected. Apparently exactly the same conditions were present even as far as the use of the same stock of KOH, but now this strength could no longer be used, but instead a 1/2% solution. With this strength a yellow color appeared which was soon gone on heating and the colorless solution seemed to have a solvent action upon the lead and copper sulphides present with the other sulphides. Prescott and Johnson 4th ed., p. 226 says "Sulphur dissolves in hot potassium hydroxide forming the thiosulphate thus: $6KOH + 4S = 2K_2S + K_2S_2O_3 + 3H_2O$". This hypo, as we found by testing, dissolves lead and copper sulphides so the effort was to prevent its formation by dissolving in 2% KOH in the cold, diluting to 1/2% and then heating. The lead sulphide dissolved. Hydrogen peroxide broke up the hypo, but as 1/2% KOH had to be used and as this will not dissolve the mixed sulphides satisfactorily, it was given up. Dissolving in 2% KOH in the cold alone, so as not to bring down the tin, caused an insoluble residue to remain behind. On testing this residue it was found to contain tin, together with lead and copper, and as it seemed to be a definite compound it was thought to be a double sulphide of tin and lead or tin and copper or both. Boiling this

double sulphide with 1/2% KOH so as not to endanger the tin, it was found that some, but not all, of the copper was taken out.

It had been noticed all along that more dilute KOH seemed to dissolve more free sulphur on heating than the strong and that more of the polysulphide, K_2S_x , was formed. As long as the polysulphide is present all sulphur is in that form, but when heated the yellow color disappears, the polysulphide being broken up and the sulphur presumably goes to form the hypo, which besides dissolving the copper sulphide and the lead sulphide also brings down the tin.

Alcohol seems to prevent the formation of the hyposulphate by forcing the free sulphur all into the polysulphide combination and keeping it there, for the yellow color remains even after long boiling. Tin, antimony and arsenic sulphides dissolve readily in alcoholic potash (5 c.c. alcohol to 50 c.c. 2% KOH) and solutions remain clear upon long heating. Oxidizing this with hydrogen peroxide, adding ammonium acetate, and then boiling with the ammonium persulphate, the tin precipitates completely, while the antimony and arsenic remain as a clear solution.

Since no exceptions came up with this proceedure, trials were made upon varying babbitt metals. In each case the alcoholic potash dissolved no lead sulphide nor copper sulphide, and with sufficient alcoholic potash and fifteen minutes extraction all tin and antimony sulphide was taken out. With a very high percent of tin present longer time should be given and more solvent used, when all can be dissolved in one extraction.

This then is the method as developed: Oxidize the acid solution of the sample with hydrogen peroxide (to change tin to the ic form), precipitate the sulphides, extract with alcoholic potash (5 c.c. alcohol to 50 c.c. 2% KOH) for fifteen minutes, two extractions may be necessary; oxidize the solution with hydrogen peroxide, add ammonium acetate (10 c.c. to keep back the antimony), add a little ammonium hydroxide to keep the solution alkaline and then add the persulphate. On boiling until the neutral point is nearly reached the tin is precipitated completely, while the antimony and arsenic remain as a clear solution ready for further separation.

Outline and Results of the Laboratory Work.

LEAD SULPHIDE.

$PbS + Na_2O_2$ = clear solution. Must be added to the warm solution drop by drop. Dry Na_2O_2 worked well.

$PbS + KOH$ = difficultly soluble.

$PbS + KOH + Na_2O_2$ = easily soluble.

PbS + dil. $KOH + H_2O_2$ - PbS changes to the insoluble sulphate.

PbS + 5% KOH on heating - some PbS dissolved	Probably due to hypo.
PbS + 2% KOH on heating - a trace PbS dissolved	
PbS + 1% KOH on heating - a trace PbS dissolved	
PbS + 1% KOH + H_2S water - no PbS dissolved	

$PbS + NH_4OH + H_2O_2$ on heating - no PbS dissolved

$PbS + K_2S_2O_3$ on heating - considerable PbS dissolved

PbS + alcoholic KOH on heating - no PbS dissolved.

ARSENIC SULPHIDE.

$As_2S_3 + Na_2O_2$ - clear solution

$As_2S_3 + KOH + Na_2O_2$ - clear solution

$As_2S_3 + KOH$ (strong) - precipitates after dissolving

As_2S_3 + dil. KOH - clear solution. Remains clear on oxidizing and acidifying with H_2SO_4, HCl, HNO_3, $C_2H_4O_2$, $C_2H_2O_4$, $C_4H_6O_6$, and upon addition of persulphate and ammonium acetate. Precipitation as $ZnAsO_4$ and $MnAsO_4$ and with magnesium mixture is complete. Easily soluble in alcoholic potash and remains clear.

ANTIMONY SULPHIDE.

$Sb_2S_3 + Na_2O_2$ - clear solution

$Sb_2S_3 + KOH + Na_2O_2$ - clear solution

$Sb_2S_3 + KOH$ (strong) - turbid solution

Sb_2S_3 + dil. KOH - clear solution. Remains clear when oxidized with H_2O_2. 2%, 1% and 1/2% KOH all dissolve the sulphide readily and without danger, on heating, of bringing down the oxide.

Sb_2S_3 + alcoholic KOH - dissolves readily to a clear solution and remains so on heating.

$K_2Sb_2O_5 + H_2SO_4$ - on boiling gives a turbid solution

$K_2Sb_2O_5 + H_2SO_4 + H_2O_2$ - on boiling gives a clear solution, by preventing oxidization, since H_2O_2 is reducing in an alkaline medium.

$K_2Sb_2O_5$ (free from H_2O_2) when acidified reduces $KMnO_4$ and KI solution, suggesting the possibility of a volumetric method for Sb.

$K_2Sb_2O_5 + KI + H_2SO_4$ - gives a curdy precipitate easy to filter,

but separation is incomplete.

$K_2Sb_2O_5$ + NH_4OH + H_2SO_4 - turbid solution.

$K_2Sb_2O_5$ + NH_4OH + H_2O_2 + H_2SO_4 - clear solution on being boiled a long time.

1st method as worked out for the separation:-

Dissolve sulphides in 1% KOH; when clear add NH_4OH, then H_2O_2; when oxidized add more NH_4OH and H_2O_2, then slight excess of H_2SO_4. The $K_2Sb_2O_5$ solution remained clear after long heating.

Amount of NH_4OH necessary:

$K_2Sb_2O_5$ + 2 c.c. NH_4OH + H_2O_2 + H_2SO_4 - on heating, clear solution.

$K_2Sb_2O_5$ + 1 c.c. NH_4OH + H_2O_2 + H_2SO_4 - on heating, clear solution.

$K_2Sb_2O_5$ + .5 c.c. NH_4OH + H_2O_2 + H_2SO_4 - on heating, turbid sol.

A very small amount of NH_4OH then is necessary to keep back the Sb.

$K_2Sb_2O_5$ + $HC_2H_3O_2$ - turbid on heating.

$K_2Sb_2O_5$ + NH_4OH + $HC_2H_3O_2$ = clear solution if enough NH_4OH has been added before acidifying.

$K_2Sb_2O_5$ + HCl = clear solution.

$K_2Sb_2O_5$ + HNO_3 = turbid solution.

$K_2Sb_2O_5$ + $C_2H_2O_4$ = clear solution.

$K_2Sb_2O_5$ + $C_4H_6O_6$ = clear solution.

$K_2Sb_2O_5$ + $ZnCl_2.NH_4Cl.NH_4OH$ = zinc antimonide; incomplete.

$K_2Sb_2O_5$ + $NH_4MnSO_4.NH_4Cl.NH_4OH$ = manganese antimonide; incomplete.

$K_2Sb_2O_5$ + $NH_4C_2H_3O_2$ and acidified with $HC_2H_3O_2$ and then $KMnO_4$, added to help the tin filtration, gave a precipitation of the antimony when in excess, probably by being reduced in the alkaline solution and forming a manganous antimonide, which is partly insoluble.

NH_4Cl was added to the antimony solution to see if chlorides had any effect on the manganese added, such as forming a manganous salt. It was found that if all the H_2O_2 was boiled off before acidifying with acetic acid, the presence of chlorides had no effect. If all the H_2O_2 was not boiled off, some of the antimony separated out and no clear solution could be obtained. This method was tried quantitatively on an alloy. The sulphides were dissolved in 1% KOH, the solution oxidized by adding NH_4OH and H_2O_2. A few more drops H_2O_2 were added, then enough $KMnO_4$ to give the ($Mn(OH)_3$ precipitate. Boil off H_2O_2 and acidify with $C_2H_4O_2$. All tin should be brought down leaving the antimony and arsenic as a clear solution. This worked all right as far as the antimony was concerned, but the $Mn(OH)_3$ did not hold back the tin upon washing.

$K_2Sb_2O_5$ + excess KOH + NH_4SO_4 + H_2SO_4 - boiling finally precipitates antimony.

$K_2Sb_2O_5$ + excess KOH + NH_4SO_4 + H_2SO_4 - not boiling does not precipitate antimony.

$K_2Sb_2O_5$ + excess KOH + $NH_4C_2H_3O_2$ + NH_4SO_4 - clear even after long boiling.

Without $NH_4C_2H_3O_2$, antimony comes down as soon as the acid point is reached, but with it the acid medium makes no difference. Only a little (5 c.c.) $NH_4C_2H_3O_2$ is necessary to keep back the antimony. Sb_2S_3 dissolved in alcoholic KOH (5 c.c. alcohol to 50 c.c. 2% KOH) and oxidized with H_2O_2, NH_4OH and $NH_4C_2H_3O_2$ added and then the persulphate, a clear solution is always the result.

STANNOUS SULPHIDE.

SnS + Na_2O_2 - dissolves and becomes turbid.

$SnS + KOH + Na_2O_2$ - clear at first; on adding Na_2O_2 becomes cloudy. K_2SnO_3 acidified with H_2SO_4: 4 trials became turbid while one remained clear. With HCl - clear when cold and hot. $SnS + KOH$ - soluble in excess on heating. H_2O_2 on boiling gives a clear solution in some cases, but more often with NH_4OH which seems to help. SnS + 1% KOH - dissolves with difficulty. H_2O_2 in an acid solution was found to be oxidizing towards Sn and can therefore be used to bring the Sn into the ic condition.

STANNIC SULPHIDE.

$SnS_2 + Na_2O_2$ - dissolves readily but gives a turbid solution. It is better to add the Na_2O_2 in solution, drop by drop, and no more than is necessary.

$Na_2SnO_3 + H_2SO_4$ - precipitation not complete.

$Na_2SnO_3 + HNO_3$ - precipitation not complete.

$Na_2SnO_3 + HCl$ - clear even after heating.

$Na_2SnO_3 + H_2SO_4$ nearly up to the neutral point and plus HCl gave a precipitate which did not dissolve on heating.

$SnS_2 + KOH$ - clear solution, also on heating. On oxidizing with Na_2O_2 solution becomes turbid. Adding the Na_2O_2 very carefully and with a little NH_4OH seems to help.

$SnS_2 + KOH + H_2O_2$ - turbid solution with strong KOH, also on adding NH_4OH and H_2O_2. Freshly prepared SnS_2 gave better results than that which had been standing.

SnS_2 + dil. KOH solution gave a clear solution which remained clear even after long boiling and adding H_2O_2.

SnS_2 + dil. $KOH + Na_2O_2$ - solution becomes turbid.

K_2SnO_3 + HCl - turbidness at first, then clear.

K_2SnO_3 + H_2SO_4 - precipitation complete.

K_2SnO_3 + HCl and then H_2SO_4 - clear cold and hot.

SnS_2 + NH_4OH + H_2O_2 - clear solution, but comes down on boiling.

K_2SnO_3 + KI + H_2SO_4 - precipitation nearly complete and difficult to filter.

K_2SnO_3 + 5 c.c. NH_4OH + H_2O_2 + H_2SO_4 - separation incomplete.

K_2SnO_3 + 3 c.c. NH_4OH + H_2O_2 + H_2SO_4 - separation incomplete.

K_2SnO_3 + 1 c.c. NH_4OH + H_2O_2 + H_2SO_4 - separation incomplete.

K_2SnO_3 + H_2O_2 + H_2SO_4 - separation incomplete.

It was therefore concluded that the H_2O_2 being used contained considerable HCl, which upon testing was found to be the case.

K_2SnO_3 + H_2O_2 + H_2SO_4 - hot - precipitation incomplete.

K_2SnO_3 + H_2O_2 + NH_4OH (any quantity) + H_2SO_4 - hot - separation complete but filtrate had a tendency to come through turbid. Precipitation in cold was the same. Since in each case H_2O_2, containing some HCl, was used and a clear filtrate was obtained with complete precipitation of tin with the H_2O_2, before adding H_2SO_4, it seems as though the HCl of the H_2O_2 prevents clear filtration. But the H_2O_2 must be added to keep back the antimony, so another acid, acetic acid, was tried for precipitation. SnS_2 dissolved in 1% KOH, NH_4OH added; oxidized with H_2O_2 and then $NH_4C_2H_3O_2$ was added to keep back the antimony before acidifying with $HC_2H_3O_2$, the tin is precipitated completely in every case. It comes down probably as the hydrate, and is hard to filter, the last additions of the wash water carrying a little of the precipitate with it.

Rapidity of filtration is not affected by precipitation in the cold or hot, and if H_2O_2 is added before acidifying, to change the hydrate to the oxide, the filtrate comes through turbid which agrees with the results using H_2SO_4 as the precipitant, the chlorine in the H_2O_2 effecting a solvent action.

$K_2SnO_3 + C_2H_2O_4$ - clear solution.

$K_2SnO_3 + C_4H_6O_6$ - clear solution.

Precipitation as zinc stannate was complete, but antimony also came down. Manganese stannate was not completely insoluble and antimony also came down with it. By reducing the $K_2Sb_2O_5$ with HI and then precipitating the tin as zinc stannate, antimony still came down, but not so much of it.

The acetic acid was, therefore, the best so far tried, since it gives complete separation and does not easily throw out the antimony. If the filtering properties could be improved it would make a neat method. It was thought that $Mn(OH)_3$ precipitated with the tin would carry the $Sn(OH)_4$ down mechanically and give the desired result. There was an improvement with its use for the filtration was more rapid than before, but the precipitate could not be washed satisfactorily without coming through turbid. The acetic acid method without the $Mn(OH)_3$ was tried on some babbitt metals; the results found as compared to other methods were low, but as only one extraction with KOH had been made the following tests were made, with the results:

Babbitt No. I. Sn - 93.22% : Sb - 3.70%: Pb - 4.11%: Cu - .41%.

1st extraction contained nearly all the tin and antimony.

2nd extraction contained a small amount of tin and antimony.

[illegible]

[illegible]

[illegible]

3rd extraction contained a trace of tin and antimony.

4th extraction contained no tin and antimony.

Babbitt No. II. Sn - 12.06%: Sb - 9.85%: Pb - 77.93%: Cu - .16%.

1st extraction contained all the antimony and tin.

2nd extraction contained none of the antimony and tin.

3rd extraction contained none of the antimony and tin.

4th extraction contained none of the antimony and tin.

These extractions were made with 2% KOH, for 15 minutes below boiling temperature. The residues treated with yellow ammonium sulphide showed no trace of tin or antimony.

An improvement upon the acetic acid method was attempted with the idea that NH_4SO_4 would cause a more granular precipitate. K_2SnO_3 + NH_4SO_4 = complete precipitation of tin when the neutral point is nearly reached and also when acid. But when acid the antimony comes down.

K_2SnO_3 + $NH_4C_2H_3O_2$ + NH_4SO_4 - complete precipitation; filters turbid in acid medium, but clear in alkaline.

$Mn(OH)_3$ was used to help filtration; it was more rapid than without the $Mn(OH)_3$, but otherwise there were no advantages over the filtration in the alkaline medium, and in either case the precipitate washed well.

Up to this time 2% KOH had been used in dissolving the sulphides, but now stannic sulphide as soon as dissolved separated out the tin oxide. It had often been wondered why, since the potassium hydroxide dissolves the sulphides of tin, arsenic and antimony so easily and is in every way clean and convenient, it was not used

instead of the other polysulphides. Here and there in the literature, hints are given as to the peculiar behavior of these sulphides towards the fixed alkalies, as for instance, F. M. Perkin XVII in speaking of the action of KOH and NaOH upon stannous sulphide says "Out of six precipitates only one dissolved; out of four, two dissolved. In a mixture of tin, arsenic and antimony sulphides, arsenic and antimony dissolved, tin did not. Sometimes the following reaction takes place, again it doesn't:

$$2SnS + 4NaOH = Na_2SnS_2 + Na_2SnO_2 + 2H_2O$$

even in the uniformity of a precipitate the same results occurred."

In following up this difficulty, it was found that impurities in the KOH used had something to do with the precipitating of the tin after solution was effected. Carbonates and sulphates in the KOH caused separation of the oxide, lime-water precipitated the tin completely, but chlorides have no effect. The main fault though lies in the strength of the caustic used, for a 1/2% solution dissolves stannic sulphide readily and does not reprecipitate any tin unless much free sulphur is present.

The fact that potassium thiosulphate is formed when KOH is heated with sulphur and that this is an important factor to be reckoned with when dissolving these sulphides, seems to be a new idea hitherto disregarded. The thiosulphate thus formed not only dissolves lead and copper sulphides, but also precipitates the tin from its solutions, so unless it is broken up in some way, or its formation prevented, the fixed alkalies cannot be used as a safe solvent for tin sulphides.

When hydrogen sulphide is passed into a solution precipita-

ting sulphides of the metals, much free sulphur is carried down mechanically. The more free sulphur present, the more thiosulphate is formed on treating the sulphides with KOH and it is very probable that the difficulties arising from its presence have been the cause of the little favor that the fixed alkalies have met with as solvents for the tin group sulphides.

The problem resolves itself therefore, into a means of preventing the formation of this hypo or of breaking it up when present. Hydrogen peroxide seemed to break up the thiosulphate and with a 1/2% KOH solution the tin remained clear for a long time, but with a 2% solution it was thrown down immediately which might have been due to the precipitating action of the sulphate formed. But a 1/2% solution is a very unsatisfactory solvent for the mixed sulphides, so other lines were followed until it was found that KOH with a little alcohol not only prevented the formation of hypo, but also allowed the use of a stronger KOH solution.

Alcoholic KOH (5 c.c. alcohol to 50 c.c. 2% KOH) dissolved the sulphides of tin, arsenic and antimony easily. A yellow solution was formed which was the same polysulphide before observed, but in this case it did not change to the colorless or, presumably hypo state on heating, but remained colored, probably owing to some peculiar action of the alcohol. This then solved the problem upon which we had been working and as the alcohol did not interfere with the complete precipitation of the tin with persulphate,- it did with acetic acid- and since in the presence of ammonium acetate the antimonate and arsenate remained clear, the method was all that could be desired.

The alcoholic KOH was tried with four Babbitt metals varying widely in composition. It was found that this solvent dissolved no lead or copper sulphide, that one extraction was all that was necessary if the amount of solvent and the time given were regulated according to the amount of tin present and that the separation was sharply defined. The amount of time given to the extraction does not seem to be regulated according to the amount of the different sulphides present, but only as to the amount of stannic sulphide in the mixture.

QUANTITATIVE WORK.

The use of acetic acid for precipitating tin was used in all the determinations, but at that time no tests had been made as to the time and number of extractions necessary and in all cases but one extraction was made. Difficulty was also experienced in washing the precipitated tin which became another source of loss.

No. I Brass Boxing.

	By Acetic acid method.	By other methods.
Unoxidized before passing in H_2S .'. probably some SnS present.	4.57% tin	7.25% tin
	3.30% tin.	7.34% tin
	5.04% tin	
	5.35% tin	
	4.64% tin	
	4.80% tin	
Oxidized –	7.52% tin	

No. II Brass Boxing.

By Acetic acid method.	By other methods.
5.61% tin	6.27% tin
6.26% tin	6.26% tin
4.94% tin	
5.5% tin	

Babbitt No. I.

Acetic acid method.	HNO_3 method.
87.45% tin	93.22% tin
87.99% tin	97.48% tin
96.83% tin	97.52% tin
94.58% tin	98.64% tin
83.1% tin	
88.5% tin	
89.6% tin	
92.5% tin	
94.5% tin	

Babbitt No. II.

Acetic acid method	HNO_3 method.
8.45% tin	14.84% tin
9.14% tin	14.86% tin

Babbitt No. III.

Acetic acid method.	HNO_3 method.
44.06% tin	48.84% tin
44.71% tin	48.82% tin

Babbitt No. IV.

Acetic acid method.	HNO_3 method.
7.15% tin	7.23% tin
8.26% tin	7.49% tin
	7.43% tin
	10.64% tin

SOLUBILITY AND BEHAVIOR OF THE SULPHIDES ON HEATING.

	Na_2O_2	KOH Na_2O_2	5% KOH H_2O_2 + NH_4OH	5% KOH	1% KOH H_2S water	½% KOH	½% KOH chlorides
PbS	clear	clear	slightly sol.	slightly	insol.	Sl. sol.	Sl. sol.
SnS	turbid	turbid	turbid	turbid	diff. sol	diff. sol.	diff. sol.
SnS_2	"	"	"	"	turbid	clear	clear
Sb_2S_3	clear	clear	"	"	clear	"	"
As_2S_3	"	"	"	"	"	"	"

SOLUBILITY AND BEHAVIOR OF THE SULPHIDES ON HEATING.

	½% KOH carbonates	½% KOH sulphates	½% KOH H_2O_2 + NH_4OH	+ NH_4OH H_2O_2 H_2S water	½% KOH $K_2S_2O_3$	alcoholic KOH (5 c.c. alcohol to 50 2% KOH)
PbS CuS	slightly sol.	slightly sol.	slight sol.	insol.	partly sol.	insol.
SnS	diff sol.	diff sol.	diff. sol.	diff. sol.	diff. sol.	clear
SnS_2	turbid	turbid	clear	turbid	turbid	"
Sb_2S_3			"	clear		"
As_2S_3			"	"		"

ACTION OF ACIDS, SALTS AND BASES UPON STANNATES, ETC., AS REGARDS COMPLETE SEPARATIONS.

	H_2SO_4	H_2SO_4 NH_4OH	H_2SO_4 H_2O_2 (Cl free) NH_4OH	HCl	HNO_3	$C_2H_4O_2$	$C_2H_4O_2$ NH_4OH	$ZnCl_2$ NH_4Cl NH_4OH (slight excess)	NH_4MnSO_4 NH_4Cl NH_4OH (sl. excess)
K_2SnO_3	complete	Complete	complete	turbid	incom.	(hard to fil) complete	(hard to fil) complete	complete	incom.
$K_2Sb_2O_5$	incom.	turbid	clear	Clear	"	incom.	clear	incom.	"
$K_2As_2O_5$	clear	Clear	clear	"	clear	clear	clear	complete	complete

	$C_2H_2O_4$	$C_4H_4O_6$	NH_4OH $C_2H_4O_2$ $Mn(OH)_3$ (Easier to fil.)	NH_4SO_4 boil until acid	NH_4SO_4 NH_4OH $NH_4C_2H_3O_2$	NH_4SO_4 NH_4OH $NH_4C_2H_3O_2$ $Mn(OH)_3$	NH_4SO_4 NH_4OH $NH_4C_2H_3O_2$ alcohol	Lime water.
K_2SnO_3	clear	Clear	complete	complete	Complete	complete	complete	complete.
$K_2Sb_2O_5$	"	"	Clear	Comes down	Clear	Clear	clear	
$K_2As_2O_5$	"	"	"	Clear	"	"	"	

REFERENCES.

I Zeitschrift für Analytishe Chemie, Vol. 27, p. 651.

II American Chemical Journal, July 1885, p. 133.

III Annalen der Chemie , Vol. 192, p. 317.

IV Zeitschrift für Analytishe Chemie, Vol. 34, p. 596.

V Jn'l. Society of Chèmical Industry, Nov. 28, 1879.

VI Chemical News, March 1888, p. 125.

VII Zeitschrift für Analytishe Chemie, Vol. 39, p. 47.

VIII Chemical News, Vol. 45, p. 101.

IX Chemical News, Vol. 46, p. 172.

X Chemical News, Vol. 77, p. 36.

XI Chemical News, Vol. 46, p. 285.

XII Chemisches Central Blatt, No. 1. - 1902.

XIII Analyst, March 1902, p. 99.

XIV Jn'l. American Chemical Society, Vol. 19, p. 935.

XV Zeitschrift für Analytishe Chemie, Vol. 34, p. 596.

XVI Jn'l. Society of Chemical Industry, Jan. 15, 1902.

XVII Jn'l. Society of Chemical Industry, May 31, 1901.